Electronic Supplementary Information

ESI-1

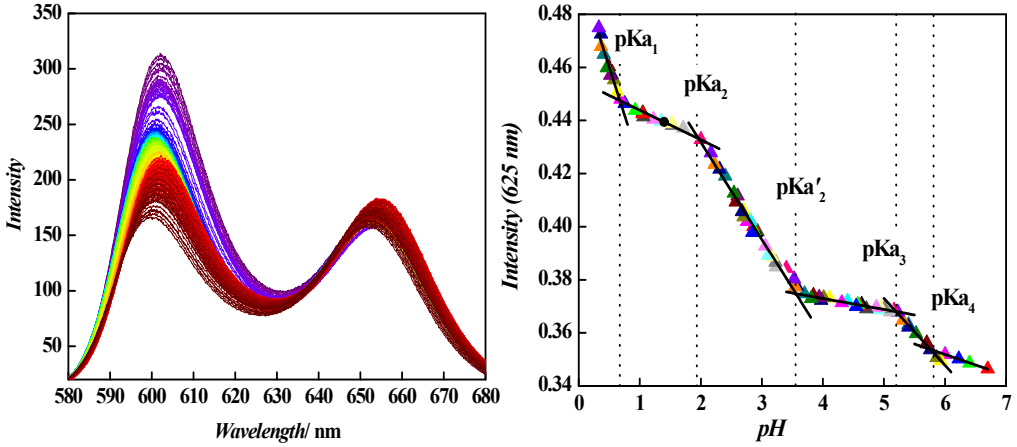


Figure ESI-1. Protolytic behavior of axial ligands of SiTCPP in CH_3CN/H_2O (8/2 v/v) observed by fluorescence spectroscopy (left) and estimation of pKa from the inflection points in the plot between fluorescence intensity at l = 625 nm and pH (right) (pKa_1 = 0.67, pKa_2 = 1.96, pKa'_2 = 3.56, pKa_3 = 5.20, pKa_4 = 5.76)

ESI-2

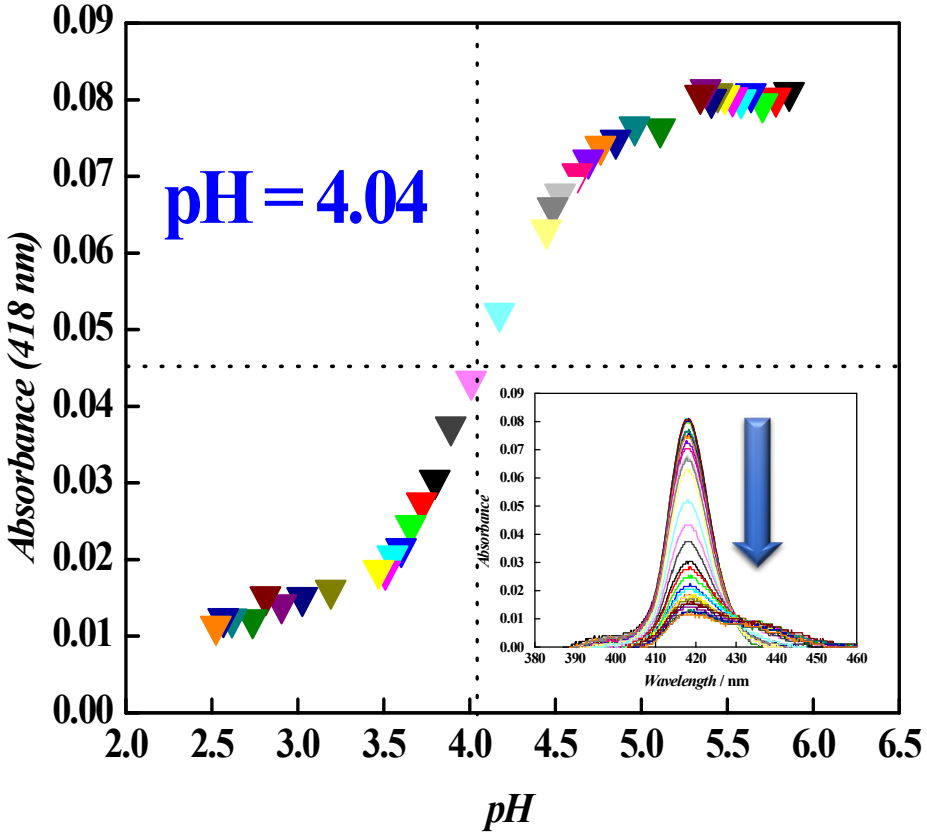


Figure ESI-2. Sudden decrease of solubility of SiTCPP in H_2O at specific pH condition (pH = 4.04): The plot of absorbance at λ = 418 nm against the pH values. The absorption spectral changes are shown in the inset.

ESI-3

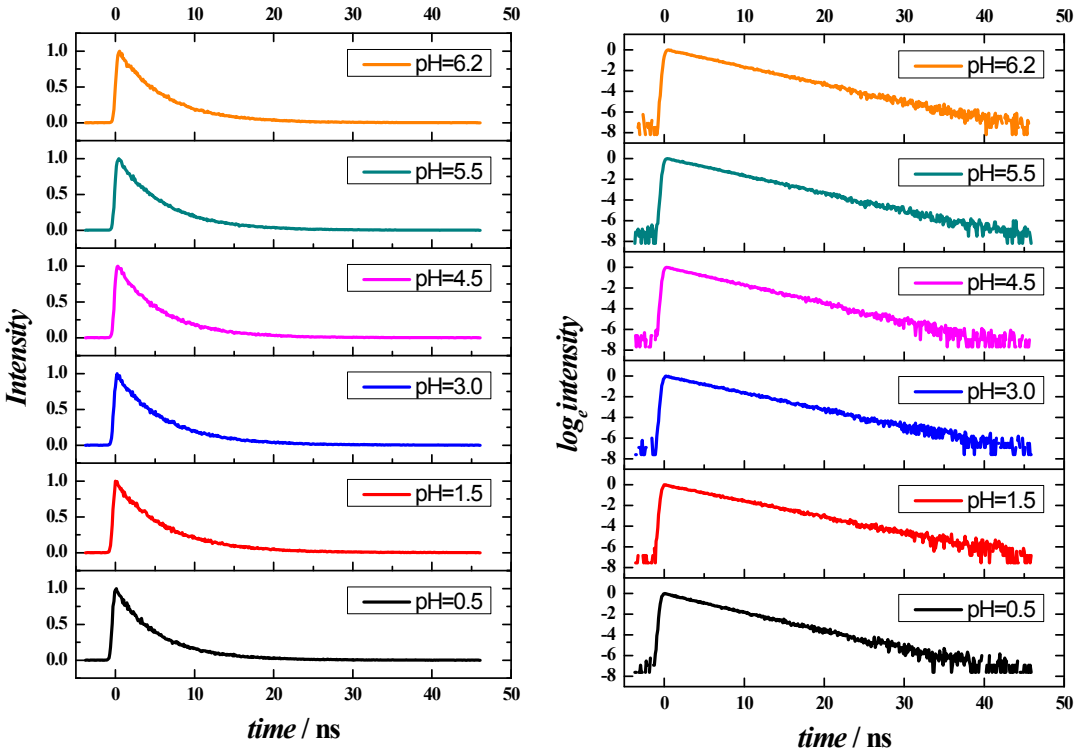
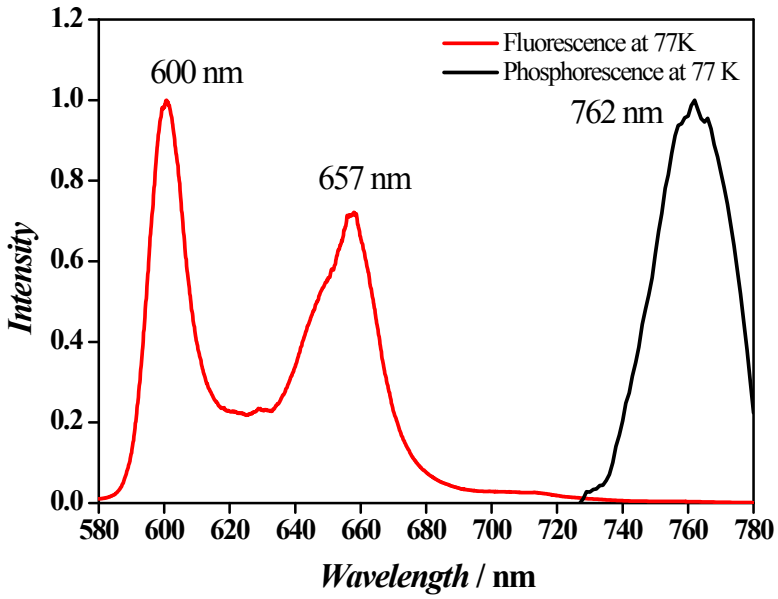


Figure ESI-3. Single exponential decay profile of fluorescence observed for SiTCPP in CH3CN/H2O (8/2 v/v) at various pH conditions, where each species in protolytic equilibria among the axial ligands exists according to the pKa values (pKa_1 = 5.76, pKa_2 = 5.20, pKa'_2 = 3.56, pKa_3 = 1.96, pKa_4 = 0.67).

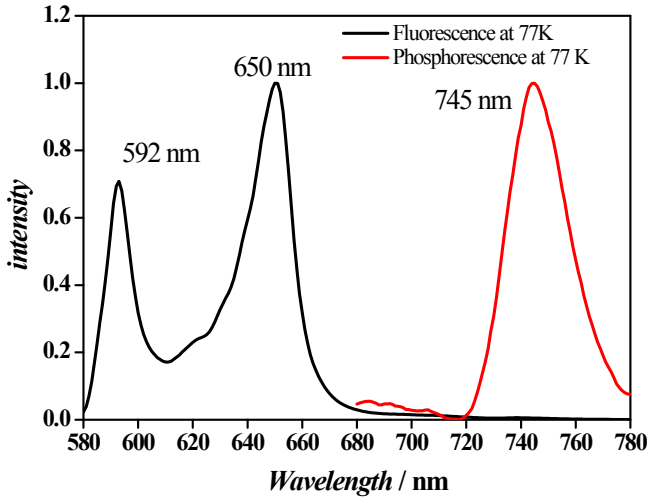
ESI-4

a) SiTCPP in Ethanol under basic condition



E_{01} = 1.63 eV

b) SiTFMPP in Methylcyclohexane



E_{01} = 1.66 eV

Figure ESI-4. Phosphorescence spectra of SiTCPP in basic ethanol at 77K and SiTFMPP in methylcyclohexane at 77 K. From their λmax, the energy of the excited triplts states of SiTCPP (1.63 eV) and SiTFMPP (1.66 eV) were determined.

ESI-5

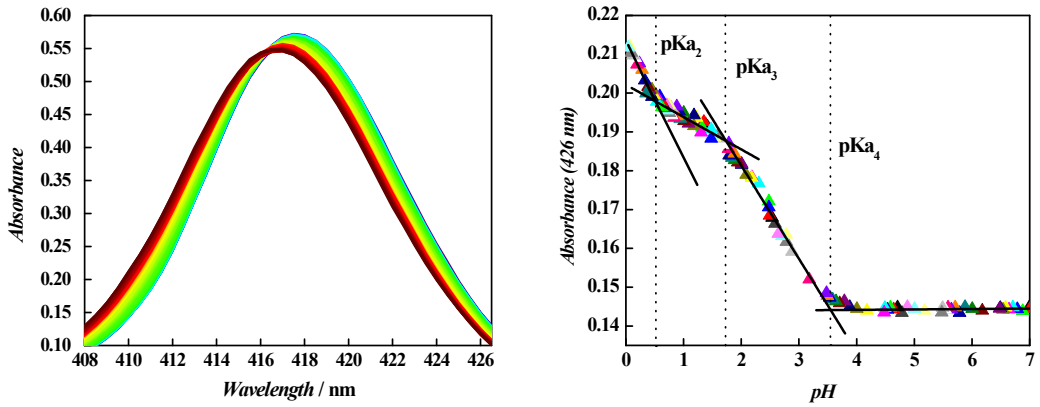


Figure ESI-5. Absorption spectra of SiTFMPP (1.2×10^{-6} M in CH_3CN/H_2O (8/2 v/v)) under various pH conditions (left) and change of absorbance in the visible absorption spectra of SiTFMPP observed at $\lambda = 426$ nm under various pH conditions(right). Three pKa's were estimated at this wavelength ($pKa_2 = 0.50$, $pKa_3 = 1.71$, $pKa_4 = 3.54$).

ESI-6

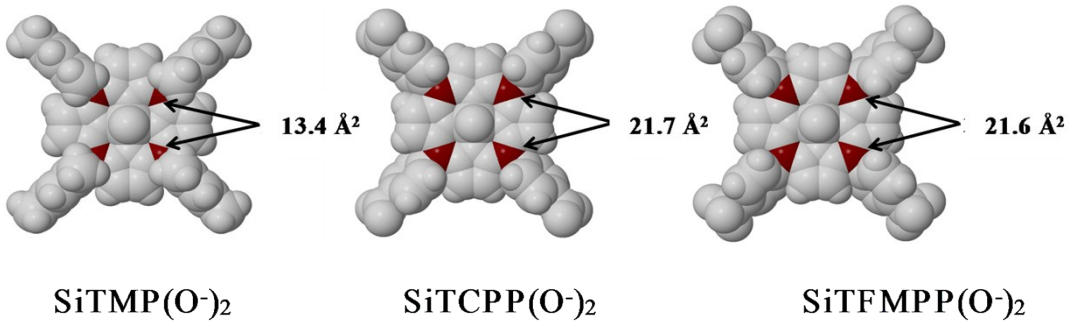


Figure ESI-6. Contact molecular surface area exposed outside of the four carbon atoms in the *meso*-position within the three Si-porphyrins: Top view of molecular structure optimized by DFT calculation with arrows indicating the carbon atoms in *meso*- position and their contact molecular surface area (Å²).